

THE PREPARATION AND PYROLYSIS OF O- AND C-BENZYLATED ILLINOIS NO. 6 COAL

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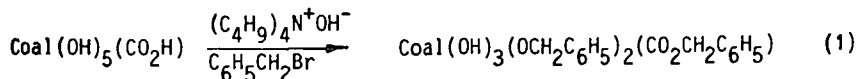
INTRODUCTION

Recent thoughtful reviews of gasification research have stressed the deficiencies in our knowledge of coal pyrolysis and the need for a greater understanding of the reactions responsible for the decomposition of coal molecules and for the formation of products.^{1,2} We have taken a new approach for the study of this issue by the pyrolysis of coals that have been modified by the introduction of labeled structural fragments. The labels were selectively introduced into the structures so that the reactions of the new structural element could be readily traced. This approach enables the reaction chemistry of a variety of different structural elements to be investigated within the environment of the coal molecules and offers great advantages for the definition of the course of the reactions in the medium, i.e. coal, that is of principal interest.

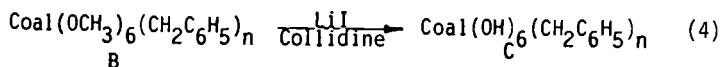
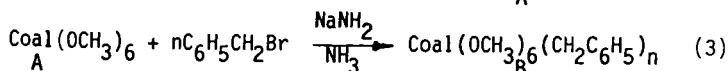
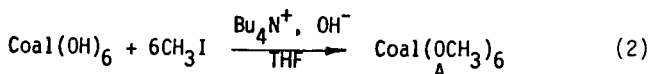
This report concerns the methods used for the selective O- and C-benylation of an Illinois No. 6 coal and the pyrolysis of these materials in a wire screen reactor.

RESULTS AND DISCUSSION

Illinois No. 6 coal was benzylated using the method described by Liotta and his coworkers.³ The extent of the alkylation reaction was controlled by limiting the quantities of base, the alkylating agent, and the reaction time. O-Benzyl, O-benzyl-d₇, and O-benzyl-1-¹³C coal were prepared using this method. The microanalytical data imply that three benzyl groups were incorporated per 100 carbon atoms of the coal. The presence of the unreacted hydroxyl groups (two to three free groups per 100 carbon atoms) and other structural features were established by infrared spectroscopy. These results are semiquantitatively in accord with the transformation shown in equation (1).



The C-benylation of Illinois No. 6 coal was carried out in three steps. Several procedures were evaluated, but the reaction sequence shown in equations (2)-(4) proved to be most suitable.



The course of each reaction was followed by infrared spectroscopy. For example, O-methyl- d_3 coal was treated with lithium iodide in collidine, no carbon-deuterium stretching frequencies were observable in the infrared spectrum of the product and the absorptions of the benzyl group appear in the C-benzylated products, B and C, whereas the hydroxyl absorption is absent in the infrared spectra of A and B, but is present in C.

The pyrolyses were carried out without difficulty in a wire screen reactor.⁴ The mass balances generally exceeded 97%. A high sensitivity GC-MS procedure was used for the determination of the important gaseous reaction products. The results are summarized in Table 1.

The char, tar, and gas yields for the pyrolysis of whole Illinois No. 6 coal obtained in this investigation are comparable with the well known data of Suuberg⁵ for whole Pittsburgh No. 8 coal. The two coals provide different amounts of char and tar, but quite comparable quantities of gas. The similarity in the total quantity of the gaseous products is also apparent when the yields of methane and carbon monoxide from these two coals are compared, Figure 1. These findings suggest that the patterns of reactivity found for the gaseous products of the Illinois No. 6 coal are representative of the behavior of other bituminous coals.

The quantities of char formed from the benzylated coals are significantly lower than the amounts obtained from the whole coals or the reaction blank at temperatures less than 800°C. On the other hand, methane and carbon monoxide are generally obtained in greater quantity from the alkylated coals than from the whole coal or the reaction blank.

The distribution of the deuterium and ^{13}C labels in the gaseous products obtained from the modified coals were studied to provide additional information about the principal reaction pathways. The yields of methane and the distribution of the label within the methane produced during the pyrolyses of the O- and C-benzylated coals are summarized in Table 2.

The pyrolysis of the exhaustively O-methylated coal, as expected, provides much more methane than the whole coal or the reaction blank at the same temperature. The enhanced yield of methane could be attributed to the low energy requirements for the cleavage of the carbon-oxygen bonds in the methyl esters and methyl aryl ethers. However, the finding that the yields of methane and carbon monoxide obtained from the O- and C-benzylated coals are also enhanced negates this simple interpretation. Only a small portion of the methane and carbon monoxide arise from the benzyl groups. Thus, the experimental results indicate that the structural modifications enhance the formation of these products in indirect ways.

The structural modifications may increase the concentration of radicals within the coal particles because the bond dissociation energies of the newly formed carbon-oxygen and carbon-carbon bonds in the modified coals are less than the bond dissociation energies of the linkages native to the coal. The radicals formed in these processes may initiate reaction sequences that lead to decarbonylation and demethylation via well known processes such as β -scission, ipso substitution and radical displacement. In addition, the O-methyl and O- and C-benzyl groups in the modified coals considerably increase the quantity of effective hydrogen atom donors within the coal particles. Productive abstraction reactions would also enhance the conversion of the macromolecular coal molecules to gaseous products.

Significantly more deuteriomethane is produced from the O-benzyl- \underline{d}_7 derivatives than from the C-benzyl- \underline{d}_7 derivatives, Table 2. This observation strongly suggests that the methyl radicals formed in the decomposition reactions of the coal molecules abstract hydrogen (deuterium) selectively from the methylene fragment of the O-benzyl group. Hence, the methyl radicals produced in the pyrolyses exhibit a reasonable degree of selectivity even at temperatures approaching 850°C. Significantly greater quantities of methane- \underline{d}_2 and methane- $\underline{^{13}C}$ are formed during the pyrolysis of the labeled O-benzylated coals than from the corresponding C-benzylated coals. Although a portion of the methane- \underline{d}_2 must arise via the exchange reactions of methane- \underline{d} , the fact that a larger quantity of methane- \underline{d}_2 is formed from the O-benzyl- \underline{d}_7 coal suggests that this labeled methane is also formed by a reaction sequence unique to the O-benzylated material. One plausible reaction pathway involves the rearrangement of the benzyloxy radical.⁶

Deuterium labeled ethene, propene, and butene are formed in readily detectable amounts during the rapid pyrolyses of the O- and C-benzyl- \underline{d}_7 coals. Similar amounts of deuterium are incorporated into the ethene produced from each coal. The most plausible reaction pathways for the formation of ethene- \underline{d} involve exchange reactions prior to the formation of ethene via pericyclic processes or β -scission reactions or subsequent exchange reactions via rapid addition-elimination reactions.

These formulations all require that the primary reactive products formed in the original decomposition reactions undergo secondary reactions within the small coal particles even in this reaction system where the secondary reactions of the stable reaction products are minimized.

The benzylation of the Illinois No. 6 coal enhances the production of benzene and toluene. The results summarized in Table 3 indicate, not unexpectedly, that the aromatic compounds are formed more efficiently from the O-benzylated coal and that the products of the pyrolysis of the O-benzyl-d₇ coal are extensively exchanged. The results can be analyzed semiquantitatively under the reasonable assumption that the hydrogen atoms of toluene formed in the reaction undergo exchange much more slowly than the hydrogen atoms of the O-benzyl group from which it is produced. This analysis suggests that about 40-45% of the O-benzyl-d₇ and 55-60% of the C-benzyl-d₇ groups experience exchange before undergoing homolysis to yield toluene at temperatures between 600 and 850°C. The difference presumably reflects the differences in the rates of the decomposition (O-benzyl > C-benzyl) which requires that the C-benzyl fragment remain bonded to the coal molecule for a longer time. These results also imply that the non-volatile coal macromolecules undergo more chemical reactions than the volatile reaction products. The results are compatible with the idea that the reactive radicals are more abundant in the plastic phase than in the rapidly cooled vapor.

CONCLUSIONS

Several conclusions emerge from the results discussed in the previous paragraphs and from other information obtained in the course of the study. First, the modified coals are generally more reactive than the unmodified starting materials. This enhanced reactivity is particularly evident in the increased yields of carbon monoxide and methane from the O-benzylated coals. The enhancement of the production of carbon monoxide suggests that the increased radical density resulting from the modification of the coal promotes other secondary radical reactions, possibly chain processes, that lead to demethylation and decarbonylation. Hence, the results strongly infer that the extent of small fragment molecule formation depends in a direct way upon the concentration of radicals within the coal particles. The enhancement of the production of methane, on the other hand, may be attributed to the increased concentration of effective hydrogen donor groups which terminate undesirable char-forming reactions. Second, the exchange patterns strongly suggest that the energetically more favorable reactions occur reversibly and that radical addition and recombination reactions compete favorably with fragmentation and radical substitution reactions. Third, the non-random distribution of the isotopic labels in the products, for example, the selective abstraction of hydrogen from the benzylic ether, indicates that the reactions underway within the coal particle are kinetically-controlled rather than

equilibrium-controlled processes even at temperature near 850°C. Fourth, the distribution of the labels in the water and ethene reveal that non-radical processes contribute significantly. Thus, theories of pyrolysis that are based exclusively on radical processes may be seriously misleading.

ACKNOWLEDGEMENT

It is a pleasure to acknowledge the support of this research by the Gas Research Institute.

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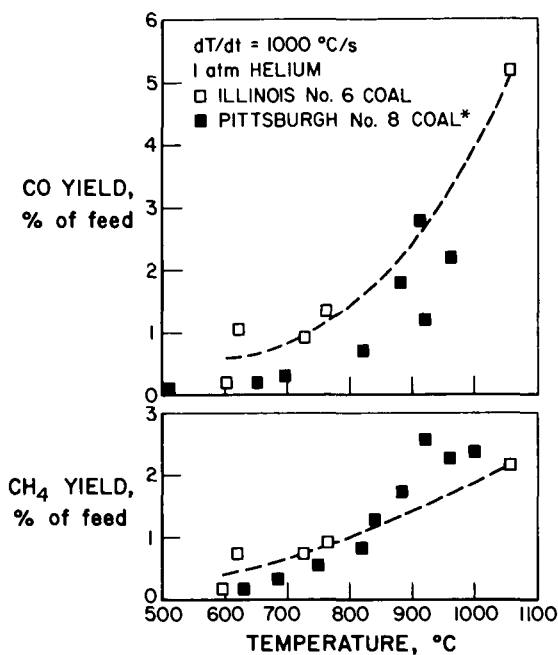


Figure 1. The yields of carbon monoxide and methane in the pyrolysis of whole Illinois No. 6 coal, open squares, and whole Pittsburgh No. 8 coal, solid squares. The data for the Pittsburgh coal were obtained by E. M. Suuberg, ref. 4.

Table 1. A summary of the results for the pyrolysis of Illinois No. 6 coal and its alkylated derivatives.

Coal type	-----Illinois No. 6-----					
Final temperature, °C	598	619	723	761	921	1057
Coal wt., mg.	11.4	14.3	7.6	12.4	5.3	9.5
Char, % of coal	78.1	70.6	59.2	56.5	55.8	50.5
Tar, % of coal	13.2	12.6	32.9	33.1	33.7	35.8
Gas, % of coal	5.9	4.2	5.4	9.6	10.5	12.6
Gas yields, wt. % of coal						
CH ₄	0.2	0.8	0.8	0.9		2.2
CO	1.2	1.1	1.0	1.4		5.2
CO ₂	1.5	0.08	1.4	0.59		1.2
H ₂ O	3.5	2.0	1.3	6.2		3.0
C ₂ H ₆	0.1	0.07	0.3	0.1		0.2
C ₂ H ₄	0.1	0.04	0.3	0.2		0.4
C ₆ H ₆	0.009	0.001	0.001	0.00		0.02
C ₇ H ₈	0.05	0.001	0.005	0.008		0.04

Coal type	-----Blank-----			--O-Methyl--	
Final temperature, °C	634	718	834	550	848
Coal wt., mg.	9.6	6.9	7.4	6.5	6.4
Char, % of coal	72.9	56.5	51.4	60.0	54.7
Tar, % of coal	9.4	20.3	21.6	27.7	23.4
Gas, % of coal	5.0	7.9	18.4	9.2	12.5
Gas yields, wt. % of coal					
CH ₄	0.2	0.9	2.4	1.8	3.4
CO	0.8	1.4	3.7	1.1	3.3
CO ₂	1.0	3.0	3.7	1.6	1.6
H ₂ O	1.5	0.8	4.4	3.6	2.5
C ₂ H ₆	0.4	0.3	0.7	0.2	0.3
C ₂ H ₄	0.2	0.5	1.5	0.3	0.7
C ₆ H ₆	0.006	0.002	0.004	0.01	0.01
C ₇ H ₈	0.01	0.0008	0.008	0.04	0.02

Table 1. A summary of the results for the pyrolysis of Illinois No. 6 coal and its alkylated derivatives.

Coal type	<u>-O-Benzyl-</u>		<u>-O-Benzyl-d₇</u>		
Final temperature, °C	532	724	508	617	745
Coal wt., mg.	13.3	13.4	10.8	13.6	10.7
Char, % of coal	60.9	53.7	68.5	57.4	51.4
Tar, % of coal	15.8	23.9	15.7	25.0	28.0
Gas, % of coal	7.8	17.2	10.3	11.8	9.7
Gas yields, wt. % of coal					
CH ₄	0.4	2.3	0.4	1.0	1.8
CO	0.7	4.4	1.0	0.6	3.1
CO ₂	3.6	4.6	3.7	1.0	1.7
H ₂ O	2.1	2.7	3.4	6.5	0.7
C ₂ H ₆	0.2	0.7	0.2	0.2	0.3
C ₂ H ₄	0.1	0.7	0.3	0.07	0.6
C ₆ H ₆	0.03	0.1	0.3	0.2	0.05
C ₈ H ₈	0.2	1.1	0.1	1.4	0.3

Coal type	<u>-O-Benzyl-1-¹³C-</u>		<u>-C-Benzyl-d₇</u>		<u>C-Benzyl-1-¹³C</u>
Final temperature, °C	840	865	611	854	758
Coal wt., mg.	3.7	3.2	9.8	8.7	7.5
Char, % of coal	51.4	50.0	67.4	51.7	52.0
Tar, % of coal	29.7	28.1	18.4	24.1	24.0
Gas, % of coal	14.1	17.6	8.9	17.2	22.7
Gas yields, wt. % of coal					
CH ₄	1.6	2.6	0.8	2.1	3.9
CO	2.5	7.1	0.6	3.3	3.8
CO ₂	3.0	2.4	0.9	2.4	0.7
H ₂ O	6.2	4.0	5.9	8.9	11.1
C ₂ H ₆	0.1	0.3	0.1	0.04	1.0
C ₂ H ₄	0.2	0.4	0.1	0.1	0.9
C ₆ H ₆	0.07	0.06	0.04	0.003	0.01
C ₈ H ₈	0.1	0.2	0.2	0.01	0.05

Table 2. The yields and isotopic composition of the methane produced in the pyrolyses of the benzylated coals.

Modified Coal	Temperature (°C)	Yield	Methane (%)			$^{13}\text{CH}_4^a$
			CH_4	CH_3D	CH_2D_2	
O-Benzyl- d_7	617	1.0	70	25	5	-
O-Benzyl- d_7	745	1.8	64	30	6	-
C-Benzyl- d_7	611	0.8	90	10	BDL	-
C-Benzyl- d_7	845	2.1	86	14	BDL	-
O-Benzyl- $\text{1-}^{13}\text{C}$	828	1.0	-	-	-	1.8
O-Benzyl- $\text{1-}^{13}\text{C}$	840	1.6	-	-	-	1.3
O-Benzyl- $\text{1-}^{13}\text{C}$	865	2.6	-	-	-	3.1
C-Benzyl- $\text{1-}^{13}\text{C}$	758	3.9	-	-	-	BDL

^aThe amount of this product in excess of natural abundance is reported

Table 3. The composition of the benzene and toluene produced in the pyrolysis of the modified coals.

	O-Benzyl-d ₇		C-Benzyl-d ₇	
	At 617°C	At 745°C	At 611°C	At 845°C
Total Yield (Weight % of coal sample)				
Benzene	0.2	0.05	0.04	0.003
Toluene	1.4	0.3	0.2	0.01
Isotopic Composition (mole %)				
C ₆ H ₆	8	10	82	40
C ₆ H ₂ D ₄	14	17	1	11
C ₆ HD ₅	70	56	15	37
C ₆ D ₆	8	8	BDL	BDL
C ₇ H ₈	BDL	BDL	5	16
C ₇ H ₃ D ₅	18	11	17	26
C ₇ H ₂ D ₆	25	25	17	20
C ₇ HD ₇	54	52	37	35
C ₇ D ₈	3	4	BDL	BDL